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TECHNIQUES OF SAMPLE ATTACK USED IN SOIL AND MINERAL ANALYSIS - PHASE I

by

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ABSTRACT

Several techniques of sample attack for the determination of radioisotopes are reviewed. These techniques include 1) digestion with nitric or hydrochloric acid in Parr digestion bomb, 2) digestion with a mixture of nitric and hydrochloric acids, 3) digestion with a mixture of hydrofluoric, nitric and perchloric acids, and 4) fusion with sodium carbonate, potassium fluoride or alkali pyrosulfates. The effectiveness of these techniques to decompose various soils and minerals containing radioisotopes such as lead-210 uranium, thorium and radium-226 are discussed.

The combined procedure of potassium fluoride fusion followed by alkali pyrosulfate fusion is recommended for radium-226, uranium and thorium analysis. This technique guarantees the complete dissolution of samples containing refractory materials such as silica, silicates, carbides, oxides and sulfates. For the lead-210 analysis, the procedure of digestion with a mixture of hydrofluoric, nitric and perchloric acids followed by fusion with alkali pyrosulfate is recommended. These two procedures are detailed.

Schemes for the sequential separation of the radioisotopes from a dissolved sample solution are outlined. Procedures for radiochemical analysis are suggested.

RÉSUMÉ

Le présent rapport examine plusieurs techniques d'attaque des échantillons pour identifier les radio-isotopes qu'ils contiennent. Ces techniques comprennent la digestion par l'acide nitrique ou l'acide chlorhydrique dans une bouteille de digestion Parr; la digestion par un mélange d'acide nitrique et d'acide chlorhydrique; la digestion par un mélange d'acide fluorhydrique, d'acide nitrique et d'acide perchlorique, et la fusion avec du carbonate de sodium, du fluorure de potassium ou des pyrosulfates alkalins. Le rapport traite également de l'efficacité de ces techniques à décomposer divers sols et minéraux contenant des radio-isotopes comme le plomb 210, l'uranium, le thorium et le radium 226.

Pour les analyses de radium 226, d'uranium et de thorium, on recommande les techniques combinées de fusion avec du fluorure de potassium, suivie de fusion avec un pyrosulfate alkalin. Cette technique garantit la dissolution complète des échantillons contenant des matières réfractaires comme la silice, les silicates, les carbures, les oxydes et les sulfates. Pour les analyses de plomb 210, on recommande la technique de digestion par un mélange d'acide fluorhydrique, d'acide nitrique et d'acide perchlorique, suivie d'une fusion avec un pyrosulfate alkalin. Ces deux techniques sont décrites en détail.

Le rapport décrit brièvement, enfin, les méthodes de séparation séquentielle des radio-isotopes obtenus à partir d'échantillons en solution et propose certaines méthodes d'analyses radiochimiques.

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PREFACE

This study was carried out under the terms of DSS Contract Number 02SQ.87055-3-4087 entitled "Analysis Of Techniques Of Sample Attack For Soil And Mineral Analysis - Phase I".

The result of the Phase I study, a literature review, is reported in this publication. The review is limited to those literatures pertaining to the techniques of sample attack of soils and minerals for the determination of lead-210, radium-226, thorium and uranium. Furthermore, it included only those techniques employing hydrochloric acid, hydrofluoric acid, nitric acid, perchloric acid, potassium fluoride, pyrosulfate and sodium carbonate.

Recommendations are made for phase II, an experimental study. Several representative samples are to be tested by all the techniques of sample attack discussed in this Phase I report.

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A. INTRODUCTION

1. Sample Attack Methods

There are many sample attack methods[1-13] available for the decomposition of soil and mineral samples. In general, they can be grouped into two: decomposition with acid, and decomposition by fusion.

Decomposition with acid is normally preferred by most analysts. It has several advantages:

(1) All acids are readily available in very pure form.

(2) No cations other than hydrogen ion is added to the solution.

(3) The reaction temperature is relatively low, e.g., from room temperature to boiling point of the acid used.

(4) The excess acid can be removed with ease by volatilization.

(5) Only glasswares or plastic wares are needed.

Decomposition with acids can be performed under oxidizing conditions using nitric acid, perchloric acid or hot sulfuric acid or non-oxidizing conditions using hydrochloric acid, hydrofluoric acid, phosphoric acid, hydrobromic acid, dilute sulfuric acid, or dilute perchloric acid. Very often, a combination of these acids are used. For very resistant samples, the acid decomposition can be performed under high pressure and temperature using a sealed tube or pressure bomb.

Decomposition by fusion with flux is generally used to decompose samples which are insoluble in acids. Fusion is very effective compared to decomposition with acids. This is due to the effect of the high temperature, which can not be achieved in an aqueous solution, and which allows heterogeneous reactions to proceed at a far greater rate. Several types of fluxes are commonly used:

(a) Alkaline fluxes include sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium peroxide, sodium tetraborate, lithium metaborate, lithium tetraborate, potassium fluoride, sodium fluoride and lithium fluoride.

(b) Acid fluxes include sodium bisulfate, potassium bisulfate, sodium pyrosulfate, potassium pyrosulfate, potassium hydrogen fluoride and ammonium hydrogen fluoride.

(c) Oxidizing fluxes include sodium peroxide, sodium nitrate and potassium nitrate.

There are several disadvantages of decomposition by fusion:

(1) Not all fluxes are readily available in high-purity form.

(2) Large amounts of cations such as Na, K, or Li are introduced into the solution.

(3) It requires fusion crucibles made of Pt, Au, Ag, Fe, Ni, Zr or silica and some of these are very costly.

(4) Corrosion of the crucible generally occurs to some extent, and frequently trace elements are exchanged between the flux and the crucible to cause contamination.

As a general rule, the choice of a sample attack method depends on the nature of the sample and the nature of the analytical work which is to follow.

2. Nature of Samples

In this study, we are concerned with the presence of four radioisotopes, uranium, thorium (Th), radium-226 (Ra-226) and lead-210 (Pb-210) in soils and minerals. Radium-226, Th-230 and Pb-210 are all members of the U-238 decay series[14] (Figure 1). Therefore, they are all associated with uranium ores, minerals and mine tailings. Radium-226 is also found in radiobarite, radiocalcite, radioopal and Mn-Fe oxides and thucholite.[5]

Uranium is distributed widely in the rocks of the earth's crust.[5,10,15] It can be found in many types of ores. The most frequently encountered ores are the hydroaluminosilicate ores, with over 50% silica, and the carbonate-hematite-magnetite ores, containing large amounts of iron (up to 70%). Other uranium ores are limestones, with over 40% calcium carbonate and coals, with over 50% carbon. The uranium in ores is present chiefly as pitchblend, uraninite, torbernite, uranophane, autunite, carnotite, coffinite, thucholite, tyuyamunite, etc. It is also found in phosphate rock, lignite and monazite sand.

Thorium is also distributed widely in the earth's crust.[5,16] The major source of thorium is monazite sand, which contains up to 30% thorium oxide. Other thorium minerals or thorium-bearing minerals are huttonite, pilbarite, thorianite, thorite, thorogummite, allanite, bannerite, euxenite, thucholite, uraninite, yttrocrasite, zircon, etc. Thorium is found mostly in the form of thorium oxide or thorium silicate in these minerals.

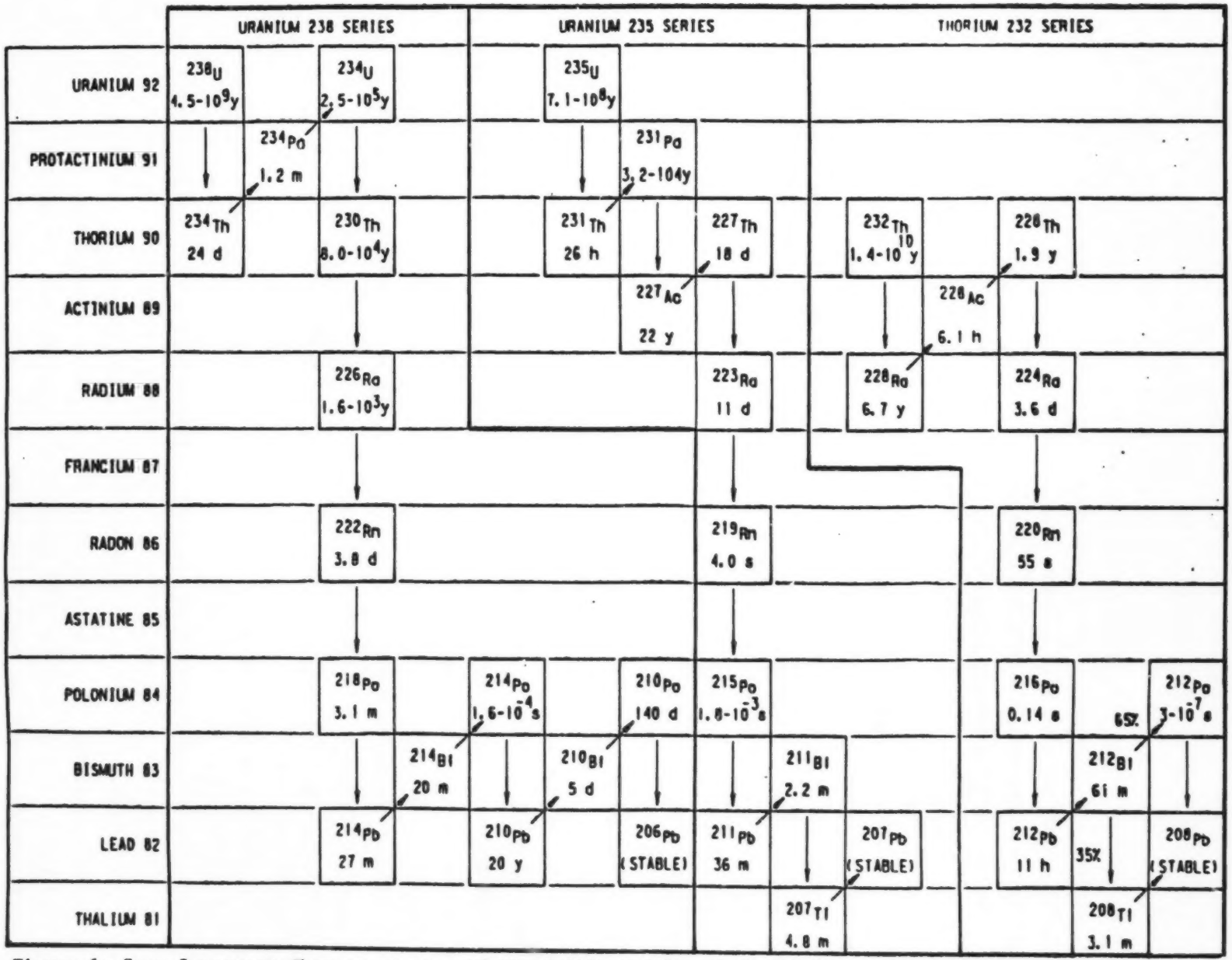

Figure 1: Some Important Characteristics Of The U-238, U-235 and Th-232 Series Decay Chains

Both uranium and thorium are associated with many other elements[5,10,15,16] such as Al, As, Be, Bi, Ca, Ce, Co, Cr, Cu, F, Fe, K, La, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, S, Si, Ta, Ti, V, W, Zn, Zr, etc. Ores that contain minerals of uranium and thorium may also contain minerals of these elements and in particular, silicon. Silicon is the second most abundant element (27.7%) in the earth's lithosphere and is exceeded only by oxygen (46.7%).[17] It is either present as silica or silicates. For example, allanite is a silicate which contains mainly of Al, Ca, Ce, Fe, and Mg. Euxenite is an oxide of Ca, Ce, Nb, Ta, Ti and Y. Zircon is mainly zirconium silicate.

3. Nature of Analysis

The acticity levels of the four radioisotopes, uranium, thorium, Ra-226 and Pb-210 present in soils and minerals can range from less than one Bq to several hundred Bq per gram. Therefore, the determination of these radioisotopes involves the measruement of constituents at weight concentrations as low as one part in 10.[12] Because of this, extremely careful attention must be placed on each and every step of the entire procedure in order to guarantee precise and accurate results. The first and the most important step is the decomposition of the sample matrix. The sample matrix must be completely dissolved and the element sought must be converted reliably to the proper ionic form before characteristic chemical reactions of that element can be obtained.

B. LITERATURE REVIEW

This chapter contains a review of the literature pertaining to the sample attack of soils and minerals for the determination or uranium, thorium, Ra-226 and Pb-210. As indicated in chapter A there are many sample attack methods for soils and minerals. However, this literature review is limited to the sample attack methods which employ hydrochloric acid, nitric acid, perchloric acid, hydrofluoric acid, potassium fluoride, sodium carbonate and pyrosulfates.

1. Decomposition with Acids

1.1 Hydrochloric Acid

Hydrochloric acid is the basic solvent in the analysis of ores and minerals. Its advantage is high volatility, and weak reducing effect on dissolution. Although hydrochloric acid is a strong acid, and its anion occurs only as a monovalent ligand, it forms rather strong complexes with the majority of metals. The most important ones are anionic complexes with the maximum coordination number and neutral complexes. This, together with the high

solubility of most of its salts in water, contributes to the high solvent capacity of hydrochloric acid.

Dilute hydrochloric acid decomposes uranium micas,[18] and uranium blacks having oxygen to uranium ratio greater than 2.7.[19] Uranium blacks are decomposition products of uraninite and crytocrystalline pitchblende of variable composition. Uranium micas are binary uranyl phosphates containing bivalent alkaline earth ion of the general formula $R^{II}(UO_2)_2(PO_4)_2.nH_2O$, such as autunite, uranocircite, saleeite and torbernite.

Minerals with a large content of tetravalent uranium and thorium are difficult to decompose by hydrochloric acid. Thus, thorianite and uranothorianite do not dissolve in the acid.[19] Thorium and rare earth phosphates, such as monazite and xenotime, are only slightly affected by concentrated hydrochloric acid. However, Purushattam[20] reported that thorite (thorium silicate) and uranothorite are decomposed by repeated evaporation with concentrated hydrochloric acid.

1.2 Nitric Acid

Nitric acid, dilute as well as concentrated, is a powerful solvent for a number of minerals, especially for sulphides and phosphates. Being a strong oxidizing agent, it converts tetravelent uranium to hexavalent uranium. Practically all oxygen-containing primary uranium minerals not combined with silica or other refractory compounds of niobium, tantalum, titanium, etc., dissolve easily in concentrated nitric acid. Secondary uranium minerals containing carbonates, phosphates, sulphates and vanadates decompose equally well.[21,22] Nitric acid may also be used to decompose organic uranium minerals such as thucholite and coal.[21]

1.3 Nitric Acid/Hydrochloric Acid

Aqua regia is a powerful oxidizing agent. It easily decomposes natural uranium oxides, uranitite and nasturane, and their numerous varieties containing rare earth elements, thorium, zirconium.[23,24] For example, cleveite, a hydrated modification with up to 12% rare earth elements, is the easiest to dissolve. When uraninite is dissolved, colloidal hydrolytic products of niobium, tantalum, titanium and tin are formed. These products absorb large amounts of thorium and negligible amounts of uranyl ion. This causes the loss of thorium when the colloidal hydrolytic products are removed by filtration. Ko and Weiler[25] reported that acid leaching of uraninite-bearing sandstones extracted as much thorium as leaching followed by fusion

of the residue with sodium carbonate. Acid leaching was by successive leachings in 8N HNO_3-0.01N $(NH_4)_2SiF_6$ and in 8N HCl-0.01N$(NH_4)_2SiF_6$. Durham and Joshi[26] decomposed environmental samples by evaporating with aqua regia three times for the determination of thorium. Dyck[26a] determined Ra-226 in soils near uranium deposits by leaching with aqua regia.

1.4 Hydrofluoric Acid/Nitric Acid/Perchloric Acid

Hydrofluoric acid differs from other halogen acids or minerals acids in three ways. Firstly, it is a very weak acid showing relatively little dissociation. In a 1N solution, only 1% is dissociated to give hydrogen and fluoride ion. Secondly, in the decomposition of minerals, hydrofluoric acid reacts with both silica and silicates and converts them to the volatile and very easily hydrolysed silicon tetrafluoride. The latter can be removed by volatilization to give a silicon-free solution. This reaction must be done in platinum or teflon containers. Thirdly, the fluoride ion forms perhaps the most stable inorganic complex with a wide variety of metal ions.

Hydrofluoric acid is seldom used alone because of the need to expel the last trace of fluorine. Boric acid is used to complex the fluoride ion and is removed by volatilization as BF_3.

Perchloric acid has the advantage that all perchlorates, with the exception of ammonium, potassium, rubidium and cesium perchlorates, are readily soluble in water. When sulfuric acid is used, the formation of insoluble sulfates can be very troublesome in subsequent analysis. Langmyhr and Sveen[27] reported the decomposition of a selection of 28 minerals with a 1:1 mixture of hydrofluoric acid and perchloric acid. The majority of these were minerals of silicate rocks. Many of these were satisfactorily decomposed at 95°C within 40 minutes (200 mg. of <100 mesh sample in 20 ml of acids) while beryl, kyanite, topaz, staurolite, pyrite, chalcopyrite and pyrrhotite were only partially decomposed after 60 minutes. Various investigators[28,34] used this mixture of acids to decompose natural silicate for the determination of lead isotopes. The samples studied include standard glasses,[28,29] tektites,[30] feldspar[31,32] and lunar samples.[33,34]

The mixture of hydrofluoric, nitric and perchloric acids is the most preferred. The addition of nitric acid helps to oxidize organic matter and sulfides, and to convert several elements into higher valence states. Larsen[35] reported the use of this mixture for the decomposition of metallic silicon, titanium, niobium,

tantalum, zirconium, hafnium and their alloys, various carbides, uranium ores and many silicates and sulfide ores. Donaldson[36] and Johnson[22] determined uranium using this three-acid mixture. Zircons and lunar samples are decomposed[37,38] by the same mixture for the study of lead isotopes. Jaworowski et al.[39] and Belt[40] decomposed surface soil and fly ash using the same acid mixture for the determination of Ra-226, Pb-210, thorium isotopes and uranium.

1.5 Acid/Parr Bomb Digestion

This method involves the decomposition in a closed container such as a Parr digestion bomb. It is simply a variant of the normal decomposition with acid to permit higher temperature, pressure and acid concentration for a longer period of reaction time. Obviously, this technique is more effective for those samples susceptible to dissolution by acid at high rather than at atmospheric pressure. However, it is generally very inconvenient and slow.

2. Decomposition by Fusion

2.1 Sodium Carbonate

Fusion with anhydrous sodium carbonate is among the most important procedures for the analysis of minerals. It is carried out almost exclusively in platinum crucibles. It decomposes most silicates, oxides, sulfates, phosphates, fluorides and carbonates. However, its action is relatively mild, leaving some considerable uncertainly as to the completeness of dissolution of refractory compounds. Green[41] reported that fusion with sodium carbonate is not sufficient to decompose even the small amount of zircon contained in igneous or sedimentary rocks. Other investigators also reported the incomplete decomposition of corundum,[42] beryl[43] and minerals containing high proportion of aluminum oxide.[43,44] Addition of borax to the sodium carbonate flux is reported to allow perfect "decomposition".[45-47] When sodium carbonate fusion is applied to large samples of siliceous materials, the silica is solubilized but requires a great deal of effort subsequently to eliminate satisfactory.[13]

2.2 Pyrosulfate

Pyrosulfate fusion is a very powerful, clean and convenient method for the dissolution of nonsiliceous refractory compounds. The flux can be prepared simply by heating sodium or potassium sulfate with an equal molar quantity of concentrated sulfuric acid. The flux is virtually a molten acid that can be used at temperatures up to nearly 800°C. The melting points of the pure potassium and sodium salts are about 300°C and 400°C, respectively. However, on heating, the pyrosulfate is decomposed with loss of sulfur trioxide, and the melting point of the mixture of sulfate and pyrosulfate increases

progressively. The high acid concentration, the high temperature available for reaction, the high concentration of sulfate ion as an inorganic complexing agent for metals, and the relatively high solubility of metallic sulfates at the high temperature used are all partly responsible for its efficiency in dissolving metallic oxides. These include refractory oxides of titanium, zirconium, thorium, niobium, tantalum, lanthanides, transuranium elements, etc., as well as all divalent and tervalent elements.[13]

The pyrosulfate fusion can be carried out in Vycor or Pyrex flasks over a blast burner without significant contamination from other than a little silica. Alternately, platinum dishes can be used but the corrosion rate becomes significant at the higher temperatures, probably because of the oxidizing power of sulfate. The reagents are available in high purity form. The dissolution of even the most refractory oxides is rapid and complete.

Pyrosulfate fusion is not effective on refractory silicates. Hence, when the latter is present in the sample, hydrofluoric acid or potassium fluoride treatment must also be used. Sill reported[48,49] the use of hydrofluoric acid, nitric acid and perchloric acid digestion followed by pyrosulfate fusion in glassware to decompose uranium ores, dusts and mill tailings for the determination of uranium, thorium, radium and lead. Talvitie et al.[50] and Kadan et al.[51] fused the insoluble residues, separated from hydrofluoric acid digestion, with potassium pyrosulfate for the determination of Pb-210.

Sill pioneered the combined potassium fluoride fusion (see 2.3 below) and pyrosulfate fusion procedure[52] for the decomposition of samples containing refractory silicates, oxides, sulfates, carbides, etc. Some of the materials that can be decomposed completely and easily include zircon, monazite sands, dunite, beryl, corundum, talc, asbestos, kaolin, fire-clay, soils, ores and many high-fired oxides and phosphates of berylium, thorium, zirconium, and aluminum.[52-54] This procedure combines the powerful action of anhydrous potassium fluoride fusion on silica, refractory silicates, metallic oxides and carbides and that of pyrosulfate fusion on metallic sulfates and refractory oxides. A sample is initially fused with anhydrous potassium fluoride in a platinum dish. This is followed by addition of concentrated sulfuric acid and transposition to a pyrosulfate fusion in the same vessel. Both fluorides and silica are volatilized simultaneously. Sample decomposition is so complete that time-consuming evaporations and filtrations are not

required. This procedure is rapid and reliable.[52-66]

2.3 Potassium Fluoride

Fusion with anhydrous potassium fluoride is probably the simplest and most effective and reliable method for the complete dissolution of a wide variety of siliceous materials. It can be carried out in a platinum vessel with little or no attack on the container, keeping contamination with foreign materials at a minimum. The high melting point of anhydrous potassium fluoride (846°C) and the high concentration of fluoride ion, which forms some of the most stable inorganic complexes with many heavy metals, both contribute to a high rate of chemical attack. Consequently, fusion with potassium fluoride is not only effective in dissolving silica and refractory silicates but most metallic oxides as well.

On heating potassium fluoride, the melt becomes progressively more alkaline due to slow but continuous loss of hydrogen fluoride produced by hydrolysis with water vapor from the air or from the combustion gases of the blast burner. Oxidation of organic materials in the flux at the high temperature of fusion is very rapid, smooth and complete, particularly in the presence of a small quantity of nitrate. With alkaline soils, pretreatment of the sample with nitric acid will fix enough nitrate to ensure the subsequent smooth oxidation of organic matter. Similarly, addition of a small quantity of potassium nitrate to the potassium fluoride before or during fusion causes rapid oxidation and dissolution of very refractory carbides such as silicon carbide.

C. DISCUSSION OF AVAILABLE LITERATURE

The literature review on the methods of sample attack revealed an interesting tendency. While each author described the method and results in detail, and compared the uniqueness of the method to others, information on the fraction of sample dissolved, fraction of element lost, length of time required, health hazards involved, interference, cost, etc., was rarely reported. The lack of this kind of information is understandable as it is highly dependent on the type of sample being analyzed, i.e., on the chemical composition of the sample, the size of the sample taken for analysis, the element or radionuclide being determined, the procedure being used subsequent to the sample dissolution for separation and measurement, and the sensitivity, precision and accuracy desired.

1. Fraction of Sample That Dissolves

The fraction of sample that dissolves depends on the chemical composition of the sample, and on the particular element or radionuclide being determined. If the radionuclide being determined is known to be hydrolytically inclined and tends to form very refractory compounds, then even 99.9% dissolution of the gross sample will not necessarily guarantee that trace quantities of that isotope will be dissolved. Thorium and many tervalent and quadrivalent ions are easily hydrolysed, even at very low hydroxide concentration. For example, both thorium nitrate and thorium chloride are very soluble in water. When these aqueous solutions are evaporated just to dryness on an electric hot plate, the residues are no longer soluble in water and they must be dissolved in concentrated acid such as nitric acid. Now, if these acid solutions are re-evaporated to dryness and the residues are dried on the electric hot plate for several hours, they will not dissolve significantly on boiling with concentrated nitric acid. This behaviour demonstrates[67] the hydrolysis of water soluble thorium nitrate and thorium chloride to thorium hydroxide and the subsequent conversion to the insoluble refractory oxide.

Conversely, as little as 1% dissolution of the gross sample might amount to virtually 100% recovery of a major constituent if that constitutent is highly soluble and the remainder is insoluble. For example, in carnotite ore, natural uranium is associated with potassium and vanadium in the form of $K_2(UO_2)_2(VO_4)_2.3H_2O$. This uranyl vanadate is acid soluble. To determine the macro concentrations of uranium in carnotite ore, one needs only to dissolve the acid soluble uranyl vanadate.

In general, the observation that a sample is "dissolved" or "not dissolved" cannot be made without specific information such as knowledge of the chemistry, chemical form, concentration, etc. of the elment being sought.

2. Fractional Losses of Each of the Radioisotopes

This is related in large part to the preceeding discussion. Uranium can be selectively leached in high yield from many of its ores in which it is present in the hexavalent state and not associated with silica. Even primary ores containing quadrivalent uranium can generally be leached satisfactorily

with concentrated nitric or perchloric acids to oxidize it to the hexavalent state. After leaching, if the residue is pure white, little uranium of significance will generally be present. On the other hand, ores containing refractory compounds of rare earths, thorium, niobium, tantalum, zirconium, etc., will require 100% dissolution to obtain quantitative recovery of even the uranium.

Thorium is a quadrivalent element known for its hydrolytic and refractory tendencies. No sample dissolution should ever be considered complete when this element (or isotopes) is being determined, unless some step is included in the sample dissolution that is known to dissolve refractory thorium compounds. Such a step is the use of pyrosulfate fusion in the absence of silica or anhydrous potassium fluoride fusion in the presence of silica. Alternately, prolonged treatment with a mixture of perchloric acid and hydrofluoric acid can be used because of the solubilizing action of fluoride ion on thorium. However, this procedure is relatively slow and must be prolonged to be completely effective.

The determination of Ra-226 and Pb-210 involves problems that might be interpreted to be incomplete sample dissolution. Although neither radium nor lead are particularly hydrolytic or refractory, they both form rather intractable, if not particularily insoluble, sulfates with the ever present sulfate. This is particularly true in the presence of the strontium and barium which occur to about 0.1%, in the earth's crust. Therefore, the procedure must ensure that such compounds are dissolved after the sample dissolution step has been completed.

The fractional losses of uranium, thorium, radium and lead will depend entirely on exactly what was done. They will certainly vary from one sample to the next, and from one procedure to the next unless the dissolution is "complete".

3. How Much Time The Procedure Takes

Procedures are difficult to categorize in terms of time required. There are many variables such as the grain size of the sample, the nature of the sample, the quantity of sample used, etc. For example, Adams reported[68] that hydrofluoric acid decomposition of silicates took five minutes at room temperature for 100 mg of simple silicates while Wilson[69] found that over 72 hours was required for the complete dissolution of 20 mg of resistant

silicates. However, in this type of sample dissolution, many samples can be digested at one time since minimal attention by an analyst is required. On the other hand, fusion with sodium carbonate requires much attention by an analyst. The actual fusion takes an average of 45 minutes to two hours or even longer and this has to be done one at a time. The fusion cake must then be disintegrated in hot water and treated with hydrochloric acid to remove the carbonate. The soluble silicic acid is rendered insoluble by evaporating the entire solution to dryness with much attendant bumping and spattering. The soluble elements are then extracted by dilute acid and filtered to remove the insoluble silica. The silica must then be volatilized with HF and the residue redissolved to recover occluded elements. All these steps are very time consuming and require constant attention. For example, the addition of hydrochloric acid must be gradual to avoid loss of sample. Also, the evaporation step is inherently slow.

In contrast, both the potassium fluoride and alkali pyrosulfate fusions are very clean and rapid. Each of these fusions requires an average of five to ten minutes to perform. The subsequent dissolution is very simple and requires no time consuming manipulations such as evaporation to dryness, filtering, etc. In the authors' laboratory, these fusions have been applied successfully to thousands of samples. They include monazite sand, pitchblend, mill tailings, fly ash, mineral, ore and environmental samples.

4. Health Hazards

The type and potential severity of the health hazards associated with the technique ought to be of little or no consequence to the selection of an analytical procedure, certainly not to the sample attack. It is not particularly more hazardous to swirl a dish containing molten potassium fluoride at 846°C than a beaker containing boiling concentrated nitric acid at 110°C. Chemistry involves calculated risks which are very small by most standards. Certainly if all safety rules and precautions are taken, the advantage of using concentrated perchloric acid far outweigh the risks of explosion. One would have to agree that dithizone extractions involving the use of cyanide as a complexant, or the wet oxidation of large samples of liver with perchloric acid pose a more severe health hazard than dissolving one gram of ore in a mixture of ten ml each of nitric acid and hydrochloric acid.

The chemicals involved in the methods of sample attack discussed in chapter B above can be grouped into three. The first is acids such as hydrochloric,

hydrofluoric, nitric, sulfuric and perchloric acids. The second is salts such as potassium fluoride, sodium carbonate, sodium sulfate and potassium sulfate. The third is a vaporized by-products such as carbon dioxide, nitrogen dioxide, sulfur trioxide and silicon tetrafluoride. Any professional chemist must treat all chemicals as toxic and hence health hazardous. All safety precautions must be observed al all times. The use of a well ventilated fumehood and appropriate safety shield for protection of eyes, face and body are mandatory. The use of gloves and laboratory coats to avoid direct and accidental contact with chemicals are strongly recommended. Avoid inhaling or breathing fumes as they are the worst enemy in the laboratory. Table 1,[70,71] tabulates information related to the health effects caused by the chemicals listed above.

5. Interference By Other Elements

The extent of interference by other elements is another characteristic that will vary markedly from one procedure to another and will require a subjective choice as to which one would rather have. No procedure will be entirely free of interferences. Precipitation of transuranium elements with cerous fluoride for alpha spectrometry is highly tolerant of relatively large quantities of iron, aluminum, titanium, zirconium, etc., while the precipitation of hydroxides from alkaline ethylenediaminetetraacetic acid cannot tolerate more than a few micrograms of all such elements combined. Is the former procedure more desirable than the latter? Not necessarily. The fluoride procedure is interferred with severely by a few micrograms of calcium or magnesium, two very common elements, while the hydroxide procedure is totally unaffected by at least 10 mg of either. It is a matter of the chemistry involved. One has to choose the one that has the greatest advantages for the purpose at hand. For instance, the choice of the method for the determination of radium-226 is influenced by the amount of barium present in the sample. The preferred method of high resolution alpha spectrometry can accommodate up to one mg of barium carrier on a 24-mm diameter source.[72-74] Degradation of the alpha spectrum already occur at 0.1 mg of barium carrier and when greater than one mg, the degradation is so serious that some other methods must be used. On the other hand, both the gross alpha and the radon emanation methods are not affected by the amount of barium present.

Table 1: Health Hazards Associated With The Chemicals Used*

	HCl	HNO_3	HF	$HClO_4$	H_2SO_4	Na_2CO_3	KF	Na_2SO_4	K_2SO_4	CO_2	NO_2	SO_3	SiF_4
Health Hazard	3	3	4	3	3	0	3	0	0	†	3	3	3
Eye Contact	B	B	B	B	B	†	†	†	†	†	B	B	B
Skin Contact	B	B	B	B	B	†	†	†	†	†	B	B	B
Swallowing	BE	B	BG	BE	E	†	F	†	†	†	†	†	†
Breathing	BE	BF	BG	B	E	†	B	†	†	M	BF	BF	BG

Health hazard rating:

0 = None, material that results in injury only under unusual conditions or by overwhelming dosage.
3 = High, short term exposure may result in major temporary or permanent injury, may threaten life.
4 = Extreme, short term exposure may result in major permanent injury or death.

Eye and skin contact, swallowing and breathing:

B = Severe irritation to corrosive effect.
E = Moderately hazardous when entering body by this route.
F = Highly hazardous when entering body by this route.
G = Extremely hazardous when entering body by this route.
M = Can result in asphyxiation.

*Compiled using information published in Ref. 70 and 71 .

†The category is not applicable or that there was insufficient data available to make a determination.

6. Special Equipment Required

All things being equal, any analyst would rather use a procedure that can be carried out in glass or plastic containers than one that requires expensive platinum dishes. However, all things are usually never equal. Generally speaking, platinum ware is not expendible, the only expense is for the original purchase. For any kind of extended program, its cost is soon amortized. When the time required for each analysis over the lifetime of an analyses program is considered, the superficial cost of the platinum ware is immaterial. Same argument for instrumentation applies. An alpha spectrometer is relatively more expensive than a gross alpha counter, but when one considers the kind of information acquired, the cost of the alpha spectrometer becomes insignificant. The apparatus commonly used for the methods of sample attack mentioned earlier are listed in Table 2.

7. Best Method Of Yield Determination

What is "best" is always conditional, depending on what the problem is, how exacting the requirements are, how much time or effort one can expend, etc. If one is doing alpha spectrometry, use of an alpha-emitting tracer of the same element being determined is best because chemical yield, counting efficiency and counting time are the same for both isotopes. For samples known to be older than 2 years, Pb-210 can be determined indirectly by measurement of its alpha-particle emitting daughter, polonium-210 (half-life 138 days). In this case, other alpha emitting polonium isotopes, Po-208 or Po-209 can be used as the tracer. For the determination of Pb-210 via its beta emitting daughter bismuth-210, an isotopic gamma emitting tracer bismuth-207 can be used. However, the latter is not readily available commercially. Therefore, one has to settle with an average chemical yield for the procedure as determined by separate analyses of standard samples.

Barium-133 is widely used as a tracer for the determination of Ra-226. Sill[74] has shown that there are differences when this tracer is used and these differences must be taken into consideration to avoid significant errors. Table 3 lists the material balance of Ba-133 and Ra-226 in a procedure for the determination of Ra-226 by high resolution alpha spectrometry (see Chapter D). The radio of Ra-226 to Ba-133 is lowest, 0.47×10^{-3}, in the final barium sulfate filtrate, while in the initial lead sulfate supernate, it is highest, 1.82×10^{-3}. This compares to 0.78×10^{-3} in the main barium sulfate precipitate used to determine this chemical yield. These results are due to the differences in the chemistry of barium and radium.

Table 2: Apparatus for Sample Attack

Method	Reaction Vessel	Heat Source
HNO_3/HCl digestion	Pyrex beaker & cover	Hot plate
HCl-Parr digestion	Parr bomb	Hot plate
HNO_3-Parr digestion	Parr bomb	Hot plate
$HF/HNO_3/HClO_4$ digestion	Teflon beaker & cover	Hot plate
Na_2CO_3 fusion	Pt. dish & cover	Blast burner, compressed air and liquified propane gas
KF Fusion	Pt. dish	Blast burner compressed air and liquified propane gas
Pyrosulfate fusion	Pt. dish or Pyrex flask	Blast burner, compressed air and liquified propane gas.

Table 3: Effect Of Divergence In Barium And Radium Chemistry On The Accuracy Of The Determination Of Radium-226 (taken from reference 74)

Fraction	Ba-133 Present (%)	Ratio of Ra-226/Ba-133 $x10^{-3}$	Change (%) Ratio	Change (%) Ra-226	Apparent Result (Bq/g)	Error %
Main $BaSO_4$	89.39	0.78	--	--	30.0	-9
$PbSO_4$ supernate	7.05	1.82	+134	+9.45	70.3	+113
$BaSO_4$ filtrate	1.29	0.47	-40	-0.51	18.0	-45
All other	2.27	0.78	0	0	30.0	-9

Correct result: 30.0 / (1 - 0.0945 + 0.0051) = 33.0 Bq/g

For the isotopic determination of uranium and thorium, U-232 and Th-234, respectively, can be used as tracers. The former is an alpha emitter and the latter is a beta emitter. For the total uranium and thorium determinations by fluorometry and spectrophotometry, respectively, the average chemical yields as determined by separate analyses of standard samples would have to be used.

8. Possibility of One Procedure

It is very difficult, if not impossible, to develop a single procedure that will permit the determination of even two or three radionucludes to say nothing of determining four as chemically different as uranium, thorium, radium and lead. In most cases, there will always be a sacrifice in sensitivity, precision, accuracy, reliability or some other desirable characteristic. Sill and his colleagues[48,55-57,60-62,64-66] have developed several procedures in which a number of radioisotopes can be determined in a single sample solution by sequential separation. These procedures all involve sample dissolution by the potassium fluoride-pyrosulfate fusion technique. In one procedure[48] in which Pb-210 is also determined, the samples is dissolved using the $HF/HNO_3/HClO_4$ digestion-pyrosulfate fusion to eliminate the possibility of loss of Pb-210 by plating onto the platinum dish.

9. Detection Limits, Precision and Accuracy

The detection limits for the determination of Ra-226, Th-232, Th-230, Th-228 and Pb-210 are dependent on the technique being used, the efficiency of the detector and the counting time. As a general guideline the detection limit for the alpha emitters using a surface barrier detector is of the order of 0.005 to 0.01 Bq. The detection limit for Pb-210 determination using indirect determination of Bi-210 is 0.02 to 0.04 BQ. The detection limit for uranium determination using the fluorometric method is generally considered to be 0.1 to 1.0 ng.

There are many factors that influence the overall precision of activity measurements by alpha spectrometry or beta spectrometry. In addition to counting precision they include sample homogeneity, reproducibility of sample positioning in the alpha spectrometer, precision of weighing and volume measurements, timing errors and instrumental dead time errors. For samples in which Ra-226 activities are low (less than 100 counts obtained) counting precision will usually be the largest contributor to the overall

imprecision. For samples whose Ra-226 activities are high (greater than 10,000 counts obtained) the contribution of the counting statistics will be negligible, i.e., less than a relative standard deviation of 1%. In these cases the contribution of the other factors to the overall analyses precision should be independently assessed. Recently four "standard" uranium tailings samples were submitted to eight Canadian laboratories for Ra-226 analysis.[75] The results show that samples analysed using alpha spectrometry gave average relative laboratory repeatibilities of 6-10% at the 3-10 Bq/g activity level and 2% at the 40 Bq/g activity level. The reproducibilities among all the participating laboratories was almost identical.

The accuracy of the radiochemical measurement of Ra-226, thorium isotopes and Pb-210 is dependent on a number of factors which include source thickness and completeness of sample dissolution. As the source becomes too thick, self absorption phenomena begin to influence the data. It is possible to make corrections for such effects[76] and should be considered with samples in which source thickness is a problem. The biggest factor influencing the accuracy of the data is the assurance of complete dissolution. Accuracy errors, caused by poor recoveries during the analysis steps, can be accounted for by the use of tracers. However, there is no way, aside from visual observation of complete solution clearness, to be aware of errors in the dissolution step. The use of "known" standards in a well defined quality control program is an important factor in accuracy assessment.

10. Cost

This will depend on variables such as sample size, digestion time, sensitivity, precision and accuracy desired, etc. Table 4 shows the cost for each of the listed methods of sample attack which are based on the following:

(1) Sample size: one gram

(2) Quantities of reagents: normally required for one gram of sample for the procedure and no allowance for repeated mutiple digestion.

(3) Purity of reagents: all reagent grade.

(4) Costs of reagents: BDH Chemicals, the only Canadian catalogue with prices still in effect as of May 1, 1984 and the price for the smallest packaging (500 ml for liquid and 500 g for solid) is used.

(5) Other costs: costs for all apparatus, utilities, etc. are not included.

Table 4: Cost Per Sample

Reagent	Unit Cost* ¢	HCl/HNO_3 Digestion	HCl/Parr Digestion	HNO_3/Parr Digestion	$HF/HNO_3/HClO_4$ Digestion	Na_2CO_3 Fusion	KF-Pyrosulfate Fusion	$HF/HNO_3/HClO_4$ Digestion-Pyrosulfate Fusion
HCl	1.89	14.3	18.9		9.5	47.3	9.5	9.5
HNO_3	3.63	9.1		36.3	18.2		1.8	18.2
HF	8.30				41.5		16.6	41.5
$HClO_4$	9.00				18.0			18.0
H_2SO_4	2.21							11.1
Na_2CO_3	4.95					49.5		
KF	12.10						3.63	
Na_2SO_4	3.53						7.1	
K_2SO_4	7.00							35.0
TOTAL ¢/ sample		23.4	18.9	36.3	87.2	96.8	81.3	133.3

*Unit cost: ¢ per ml for acids and ¢ per g for salts

D. RECOMMENDED PROCEDURES FOR SAMPLE ATTACK AND ANALYSIS

1. Methods of Sample Attack

As indicated earlier, for any chemical determination, it must be ensured that the sample matrix is completely dissolved. To choose the "best" method for sample attack may or may not be an easy task. On one hand it is easy to choose a simple acid digestion method for dissolution of carnotite when the measurement of macro concentrations of uranium and vanadium is required. This is so because carnotite is a mineral of uranyl vanadate, which is easily soluble in acid and not associated with silica (see Chapter C, 1). However, when the sample may contain refractory materials and the elements sought are in trace levels, the method chosen must be able to dissolve the most resistant mineral. The method must be time-proven to be reliable. Sill's procedure of potassium fluoride-pyrosulfate fusion[52,60,62,64] is the most preferred. This procedure "guarantees" the complete dissolution of all refractory materials. The solution from this procedure can be used for the determination of not only U, Th, Ra-226 but also Ac, Pa, and all transuranium elements.[52-66] Lead-210 can not be measured in this solution as it is partially plated on the platinum dish used for the fusion.[49] Thus, a separate dissolution procedure must be used for Pb-210.[48,49] Hydrofluoric-nitric-perchloric acid digestion followed by pyrosulfate fusion is recommended. In the event that sample size is limited to one dissolution, then this procedure can be used if U, Th, Ra-226, Pb-210 are all required.[48]

The potassium fluoride-pyrosulfate fusion procedure was originally published in 1961 by Sill[52] and has been used in his laboratory and others (including the present authors'). The experience has been of excellent results. This combination of two of the most powerful methods of sample attack available results in a procedure that is extremely effective for dissolution of the most refractory and intractable samples to be encountered. The procedure is rapid and reliable, and gives very low blanks. The mere fact of having carried out the fusion successfully is itself inherent proof that all compounds present have been dissolved completely. This procedure has been applied to many different samples for the determination of radioisotope of radium, thorium, actinium, uranium and all transuranium elements with excellent results.[52-66] An example is the determination of plutonium in soil.[77] Many laboratories simply leached the soil with hydrochloric and/or nitric acid[77-82] or fused it with sodium carbonate.[83] The results were frequently low and erratic. Occasionally,

reproducible results were obtained, but by analyzing the insoluble residue remaining after leaching, the results were shown to be low. The analysts ignored the fact that plutonium oxide becomes extremely refractory and difficult to dissolve when it is heated strongly, or ignited in the laboratory to burn off organic material prior to analysis. Sill, Puphal and Hindman[60] dissolved 10 g of soil spiked with known quantities of various alpha-emitting radioisotopes using the potassium fluoride-pyrosulfate fusion procedure. Then, sequentially separated Th-230, Pa-231, U-233, Np-237, Pu-239, Am-241, Cm-244, and Cf-252 for analysis by alpha spectrometry. In that study, tracers were used to follow the distribution of activity in every step of the entire separation scheme. Even the activities retained in the beakers, separatory funnels, filtrates, etc., were determined. The results of this study are shown in Table 5. As can be seen the material balances and chemical yields are remarkably high. For example, the material balance and chemical yield for Th-230 are 99.5% and 98.5% respectively, for U-233, 100% and 94.1% and for Pu-239, 99.2% and 99.2%. These high chemical yields could not have been possible if the potassium fluoride-pyrosulfate fusion failed to dissolve the sample completely. Percival and Martin[61] developed a scheme in which Ra-226, Ra-228, thorium isotopes and Pa-231 in environmental and process waste samples were separated sequentially. The solid samples were dissolved by the potassium fluoride-pyrosulfate fusion procedure. Tracers were used for chemical yields and material balances. The extremely high yields, i.e., 99±1%, 97±2%, and 96±2% (Table 6) for radium, actinium and thorium, respectively, indicated that the sample dissolution was complete.

The hydrofluoric/nitric/perchloric acid digestion-pyrosulfate fusion was used by Sill and Willis[49] to decompose uranium ores and air dusts for the determination of Pb-210.[48] Since no suitable isotopic tracer for Pb-210[48] was available, a standard pitchblend was also analysed using the identical procedure. This standard pitchblend has been shown by extensive previous work[60,61,84,85] to be in true equilibrium and of accurately known activity. The results of the standard pitchblend 6.02, 6.08, and 6.04±0.07 x 10^3 dpm/g were in exact statistical agreement with the known value of 6.06±0.04x10^3 dpm/g. This indicated an average chemical yield of greater than 98%. This same procedure was also used to decompose uranium ores, dusts and mill tailings for the simultaneous determination of U-238, U-234, Th-230, Ra-226 and Pb-210.[48] The chemical yields were all shown to be greater than 85%.

Table 5: Distribution of Activity in Analysis of Ten Grams of Soil (taken from reference 60).

	Radionuclide present, %							
	Th-232	Pa-231	U-233	Np-237	Pu-239	Am-241	Cm-244	Cf-252
Platinum Dish without Rinsing	0.03	0.02	0.31	0.04	0.09	0.05	0.04	0.05
Main $BaSO_4$ after Reprecipitation	(99.92)	(99.84)	(99.25)	(99.83)	(99.83)	(98.67)	(96.09)	(82.63)
800-ml beaker from main $BaSO_4$ precipitation	0.01	0.03	0.34	0.06	0.01	0.30	0.07	0.19
Second $BaSO_4$ (3 additional portions of $BaCl_2$)	0.01	0.04	0.02	0.01	<0.01	0.52	2.21	8.21
Main filtrate after second $BaSO_4$ precipitation	<0.01	<0.01	<0.01	<0.01	<0.01	0.12	0.96	7.46
Filtrate and wash from reppts of main $BaSO_4$	0.02	0.04	0.06	0.03	0.04	0.34	0.63	1.43
250-ml Erlenmeyer from reprecipitation	0.01	0.03	0.02	0.03	0.03	<0.02	<0.02	0.03
150-ml Beaker from Aluminum Nitrate Fusion	0.01	0.32	<0.01	<0.01	<0.01	0.04	<0.02	0.02
First Aliquat-336 Extract before Scrubbing	(99.76)	(96.00)	(98.51)	(97.12)	(99.53)	(2.72)	(1.19)	(2.70)
First 10-ml 8*M* HNO_3 scrub	0.06	2.43	1.01	0.35	0.01	2.63*	1.13*	2.62*
Second 10-ml 8*M* HNO_3 scrub	0.07	2.16	1.26	0.40	0.01			
Third 10-ml 8*M* HNO_3 scrub	0.06	2.18	1.25	0.37	0.01			
First 50-ml 10*M* HCl scrub after 10-ml ext'n	67.97*	0.004	0.02	0.01	0.01	0.09	<0.05	<0.02
Second 50-ml 10*M* HCl scrub after 10-ml ext'n	26.20*							
Third 50-ml 10*M* HCl scrub after 10-ml ext'n	3.42*							
10-ml extract of combined HCl scrubs	0.79	0.12	0.74	0.41	0.17	(<0.01)	(<0.01)	(<0.01)
First 50-ml $HClO_4$ strip	0.30	(87.29)	(92.35)	(93.59)	(96.72)			
Second 25-ml H_2O strip	0.03	1.12*	1.74*	1.90*	2.50*	<0.02	<0.02	<0.02
Residual organic phase after two strips	<0.01	0.49	0.12	0.06	0.08	<0.02	0.06	0.08
Separatory funnel	<0.01	0.22	0.02	0.03	0.02			
Residual $Al(NO_3)_3$ after First Extraction	(0.13)	(3.52)	(0.74)	(2.71)	(0.30)	(95.91)	(94.90)	(79.91)
Pa-(U)-Np-Pu Fraction from First $HClO_4$ Strip	(0.30)	(87.29)	(92.35)	(93.59)	(96.72)	(<0.02)	(<0.02)	(<0.02)
Main $BaSO_4$ precipitate	(0.30)	86.00*	92.09*	94.00*	95.60*	(<0.02)	(<0.02)	(<0.02)
Filtrate and washes from $BaSO_4$ precipitation		0.06*	0.03*	0.66*	0.04*			
250-ml flask, centrifuge tube, and ethanol transfer liquid from final $BaSO_4$ pptn		0.08*	0.28*	0.06*	0.25*			
Thorium Fraction from Combined HCl Scrubs	(98.47)	(0.004)	(0.02)	(0.01)	(0.01)	(0.09)	(<0.05)	(<0.02)
Main $BaSO_4$ precipitate	(98.05)	(0.004)	(0.02)	(0.01)	(0.01)	(0.09)	(<0.05)	(<0.02)
Filtrate and washes from $BaSO_4$ precipitation	0.07*							
250-ml flask, centrifuge tube, and ethanol transfer liquid from final $BaSO_4$ pptn	0.35*							
Second Aliquat-336 Extract before Scrubbing	(0.13)	(2.49)	(0.74)	(2.81)	(0.30)	(94.43)	(93.76)	(79.41)
Three 16-ml 10.8*M* NH_4NO_3 scrubs combined	0.01	0.04	<0.01	0.17	<0.01	0.82	0.90	1.00
First 30-ml 8*M* HNO_3 strip	<0.01	0.02	<0.01	0.07	<0.01	(92.05)	(91.43)	(77.23)
Second 10-ml 8*M* HNO_3 strip						1.40*	1.43*	1.16*
Residual organic phase after strips	0.12	2.25	0.74	2.27	0.30	0.16	<0.02	0.02
Residual $Al(NO_3)_3$ after Second Extraction	<0.01	1.03	<0.01	0.20	<0.01	1.48	1.14	0.50
Tervalent Actinides from First 30-ml HNO_3 Strip	(<0.01)	(0.20)	(<0.01)	(0.07)	(<0.01)	(92.05)	(91.43)	(77.23)
$Ce(OH)_3$ precipitate	(<0.01)	(0.20)	(<0.01)	(0.07)	(<0.01)	92.14*	90.16*	77.10*
Filtrate from $Ce(OH)_3$ precipitate						0.17*	0.06*	0.17*
Water and ethanol washes of $Ce(OH)_3$						<0.02*	0.04*	0.14*
Centrifuge tube and beaker from $Ce(OH)_3$						0.04*	0.07*	0.12*
Material balance[a]	99.84	98.85	100.05	101.13	99.17	100.30	98.90	100.30
Recovery of each nuclide[b]	98.47	88.41*	94.09	95.49	99.22	96.08	93.99*	81.01*

[a] Sum of all measured fractions. [b] Fractions indicated by asterisks combined as recommended in the general procedure. Indicated recovery and calculated values given in parentheses have been corrected for the difference in material balance from 100%. * Recoveries increase to 94.30% and 89.25% for curium and californium, respectively, with three additional portions of barium chloride, and to about 97% for protactinium in the absence of citric acid.

Table 6: Distribution of Activity in a Procedure for Sequential Determination of Radium, Actinium, and Thorium (taken from reference 61)

	Element Present, %		
Fraction	Ra	Ac	Th
First $PbSO_4$ supernate	0.6	0.2	0.6
Second $PbSO_4$ supernate	≤0.1	≤0.1	≤0.1
$PbSO_4$ wash	≤0.1	≤0.1	≤0.1
Reprecipitated $BaSO_4$	99±1	1.0	
Combined $BaSO_4$ supernates	0.3		
Aqueous after Ac extraction		0.6	
Combined washes of Ac extract		0.4	0.1
Ac organic after strips		0.5	0.7
$Ce_2(C_2O_4)_3$ supernates and wash		0.3	
$Ce_2(C_2O_4)_3$ precipitate		97±2	
Aqueous after Th extraction			0.4
Combined washes of Th extract			0.2
Th organic after strips			0.2
Separatory funnel and stopper			0.8
$BaSO_4$ supernates and wash			0.9
$BaSO_4$ precipitate			96±2
Aqueous after Th electrodeposition			1.0
Electrodeposition plate			96±2

1.1 Recent Experience With Recommended Methods

As indicated in chapter B each of the sample attack methods has its own capabilities. For example, hydrochloric acid, nitric acid and their mixture can leach out those constituents that are soluble in the acids. They are not effective if the sample is associated with silica. Hydrochloric or nitric acid in Parr bomb can't attack silica either. Hydrofluoric acid must be used when silica is present. It is very effective for many refractory oxides as well as silicates. However, the completeness of the sample dissolution depends on the size and type of sample. Refractory silicates such as clay or large samples of some refractory oxides are dissolved so slowly that prohibitive lengths of time are required. Fusion with sodium carbonate dissolves most silicates and oxides. However its action is relatively mild and the subsequent removal of soluble silicate is awkward and time consuming. Pyrosulfate fusion is extremely powerful for nonsiliceous refractory materials. It is very clean, easy to handle and rapid. Potassium fluoride fusion is not only effective for silica refractory silicates but also refractory oxides and carbides. It is also very clean, easy to handle and rapid. Therefore, if silica or refractory silicate and refractory oxides, etc. are present, a combination of potassium fluoride-pyrosulfate fusion or hydrofluoric-nitric-perchloric acid digestion-pyrosulfate fusion is mandatory.

CANMET sponsored two interlaboratory studies recently. One was for the determination of Ra-226 in uranium and uranium/thorium ores BL-4A, BL-5, DH-1a and DL-1a for the Canadian Certified Reference Materials Project (CCRMP),[86] and the other was the determination of Ra-226, Ra-228, Th-228, Th-230, Th-232, Pb-210, Po-210 and Pa-231 in uranium tailings reference materials UTS-1, UTS-2, UTS-3 and UTS-4 for the National Uranium Tailings Research Program (NUTP).[75] To dissolve these ores and tailings, most laboratories used a combination of either the potassium fluoride-pyrosulfate fusion or the hydrofluoric-pyrosulfate fusion procedure (Table 7). Hydrofluoric acid digestion was also used or in combination with other fusions such as lithium metaborate and lithium tetraborates. The results of the NUTP study are summarized in Table 8.

1.2 Time Required For Recommended Methods

The amount of time it takes for sample attack should not be an important consideration when selecting a particular procedure. It depends on many variables such as size of sample, type of sample, and how many samples are

Table 6: Sample Attack Methods Used in the CCRMP and NUTP Studies*

Isotope	No. of Labs	[KF-Py]	[HF-Py]	[HF-A]	[HF-F]	[Na_2CO_3]
CCRMP						
Ra-226	11	3	3	2	2	1
NUTP						
Ra-226 Ra-228	7	2	3		1	1
Th-228 Th-230 Th-232	8	3	3	1	1	
Pb-210	7	2	2	3		

[KF-Py] Potassium fluoride-Pyrosulfate fusion

[HF-Py] HF/HNO_3/$HClO_4$ digestion-Pyrosulfate fusion

[HF-A] Digestion with HF, HNO_3 and $HClO_4$ or H_2SO_4

[HF-F] HF digestion and fusion with other than pyrosulfate

[Na_2CO_3] Na_2CO_3 fusion

*compiled from data in Ref. 75 and 86.

Table 8 Consensus Values for Isotope Activities in Tailings Reference Materials (taken from Ref. 75)

Isotope	Consensus value (CL), Bq/g			
	UTS-1	UTS-2	UTS-3	UTS-4
Th-230	3.6 [3.0 - 4.2]	4.4 [3.3 - 5.5]	11.3 [10.5 - 12.1]	22.9 [20.3 - 25.5]
Ra-226	3.67 [3.52-3.82]	5.6 [5.2 - 6.0]	13.3 [12.7 - 13.9]	38.6 [36.2 - 40.9]
Pb-210	3.36 [3.15-3.58]	4.6 [3.9 - 5.3]	12.6 [11.7 - 15.5]	34.7 [30.4 - 39.0]
Po-210	3.1 [2.7 - 3.5]	4.4 [3.7 - 5.1]	11.8 [10.8 - 12.9]	30.8 [25.8 - 35.9]
Th-232	.68 [.59- .77]	.88 [.67- 1.08]	(.16± .04)	(.48± .06)
Ra-228	.68 [.47- .89]	1.0 [0.7 - 1.4]		
Th-228	.71 [.58- .84]	.92 [.58- 1.25]	(.16± .04)	(.23± .04)
Pa-231	(.21± .03)	(.37± .05)	(.70± 1.0)	(2.4 ± .3)

(CL) = statistical uncertainty range at 95% confidence level.

Square brackets are low and high values

Round brackets are single laboratory results and uncertainty estimates

done at the same time, etc. The potassium fluoride fusion and the pyrosulfate fusion take a very short time. For example, a potassium fluoride fusion on one gram sample takes seven to 10 minutes. This includes the time required to heat the flux from room temperature to the melting point of 846°C. The pyrosulfate fusion also takes seven to 10 minutes. For a complete potassium fluoride-pyrosulfate fusion procedure, it takes 15 minutes for pretreatment with tracer(s), nitric and/or hydrofluoric acid, 10 minutes for potassium fluoride fusion, 60 minutes for sulfuric acid transposition, 10 minutes for pyrosulfate fusion and 15 minutes for dissolving the fusion cake in dilute hydrochloric acid. A total of less than two hours. The final solution is perfectly clear[13,52] which indicates complete sample dissolution. No filtration is necessary. The 60 minutes for the sulfuric transposition does not require any work other than occasional attention. Therefore, when a set of ten or more samples are fused, the sulfuric acid transposition of the first sample is complete and ready for the pyrosulfate fusion, by the time the potassium fluoride fusion is finished on the last sample. In the authors' laboratories, routine dissolution of a set of 12 samples can be completed in four hours excluding time required for weighing of samples and reagents or cleaning and decontaminating the platinum dishes.

For the hydrofluoric/nitric/perchloric acid digestion-pyrosulfate fusion procedure, the deciding factor is the length of time it takes to complete the acid digestion. The pyrosulfate fusion and subsequent dissolution in dilute acid takes 20 minutes.

1.3 Potassium Fluoride-Pyrosulfate Fusion Procedure[87]

1.3.1 Apparatus

Platinum dishes: evaporating type, 40 or 50-ml, approximately 50-mm diameter by 25-mm high, Englehard Model 102 or equivalent (normal crucibles do not work).

Crucible Tongs: Platinum tipped, Englehard model 506

Blast burner: 4-cm grid diameter with air and gas inlets, Fisher model 03-910-5 or equivalent.

Ring stand and support.

Plastic stirring rods: 3-mm diameter by 10-cm long, rounded ends.

Hot plate: Teflon coated with 40-cm x 80-cm heating surface, Westblend model 240 or 320 (available at most department stores) or equivalent.

Gas: Liquified propane.

Beakers: Pyrex, 250-ml.

Watch glasses: 80-mm diameter

Fumehood: Constructed of #316 stainless steel with wash down capabilities to clean the blower, exhaust ducting and interior working area.

Tissue wipers: 1 ply, 22-cm x 12-cm, Kimwipes #57-210 or equivalent.

1.3.2 Reagents

Nitric acid (16M): Reagent grade.

Hydrofluoric acid (50%): Reagent grade.

Sulfuric acid (18M): Reagent grade

Potassium fluoride (ANHYDROUS): Reagent grade.

Sodium sulfate (anhydrous): Reagent grade.

Silica gel: Reagent grade.

Tracers:

1.3.3 Methodology

WARNING - Wear face shield, rubber gloves and protective clothing.

(1) Weigh 1.00 g of 100 mesh sample in a 40-ml platinum dish.

(2) Wet sample with 0.5 ml of 16M HNO_3, and warm gently at 100°C on a hotplate until the chemical reaction and frothing have ceased.

(3) Add 1.00 ml each of tracers and evaporate just to dryness. Do not bake the residue.

(4) Add 2 ml of 50% HF and evaporate just to dryness.

(5) Sprinkle 3 g of anhydrous KF uniformly over the residue and mix with a plastic stirring rod. Remove all particles adherring to the rod with half a piece of tissue wiper, crumple it into a ball and place it in the platinum dish.

(6) Carefully ignite the tissue and fuse over a blast burner until the KF melts. This step takes approximately 4 to 5 minutes. If the melt is turbid or highly colored, add 250 mg of pure silica get and continue heating to a clear melt.

(7) With a pair of crucible tongs, grasp the ouside walls of the dish, roll the melt around the upper walls. The tips of crucible tongs should NEVER be in contact with the inside walls of the platinum dish.

(8) Resume heating until a clear melt is obtained and continue for 2 minutes.

(9) Cool to room temperature, add 4.5-ml of 18M H_2SO_4 and warm gently on a hot plate until the KF fusion cake dissolves completely.

(10) Heat over blast burner carefully until copious amounts of H_2SO_4 fumes are evolved.

(11) Add 2 g of anhydrous Na_2SO_4 and continue heating until a clear pyrosulfate melt is obtained.

(12) Use crucible tongs to grasp the outside walls and roll the melt to the upper walls to dissolve any remaining particles.

(13) Cool to room temperature, flex the walls to break loose the cake and place it in a 250-ml beaker.

(14) Add 35 ml of boiling 5% HCl to the dish and leave it on the hot plate for a few minutes to dissolve any cake remaining in the dish. Roll the solution carefully to reach the upper walls.

(15) Pour the solution into the beaker containing the main portion of the fusion cake and place beaker on the preheated hot plate.

(16) Hold the dish upside down, rinse the inside walls with 15 ml of boiling 5% HCl, using a disposable pipette, into the beaker directly. Make sure that hot rinses reach all parts of the inside walls by rotating the dish. Use "rubber fingers" to protect hands. The platinum dish should not be placed in the beaker.

(17) Cover the beaker, boil and swirl to dissolve the cake completely.

(18) Cool to room temperature and add 50 ml of deionized water.

(19) Proceed to Ra-226, isotopic thorium, total thorium, isotopic uranium or total uranium determination.

1.4 HF/HNO_3/$HClO_4$ Digestion-Pyrosulfate Fusion Procedure

1.4.1 Apparatus

Fumehood: For perchloric acid use only, constructed of #316 stainless steel with wash down capabilities to clean the blower, exhaust ducting and interior working area.

Hot plate: Teflon coated with 40-cm x 80-cm heating surface, Westbend model 240 or 340 (available at most department stores) or equivalent.

Teflon beakers: 100-ml made of virgin teflon TFE or teflon PFA.

Teflon watch glasses: 65-mm diameter

Beakers: Pyrex, 250-ml.

Watch glasses: 80-mm diameter.

Erlenmeyer flasks: Pyrex, 250-ml, wide-mouth.

Blast burner: 4-cm grid diameter with air and gas inlets, Fisher model 03-910-5 or equivalent.

Flask tongs: Fisher model 10-062 or equivalent.

1.4.2 Reagents

Hydrofluoric acid (50%): Reagent grade.

Nitric acid (16M) Reagent grade.

Perchloric acid (70%): Reagent grade.

Hydrochloric acid (12M): Reagent grade.

Sodium sulfate (anhydrous): Reagent grade.

Lead-bismuth carrier (1 mg each of lead and bismuth per ml): Dissolve 160 mg of $Pb(NO_3)_2$ and 232 mg of $Bi(NO_3)_3.5H_2O$ in 10 ml of 2M HCl and dilute to 100 ml.

1.4.3 Methodology

(1) Weigh 1.00 g of 100 mesh sample into a 100-ml teflon beaker.

(2) Add 5 ml each of 16M HNO_3 and 50% HF, 2 ml of 70% $HClO_4$, 1.0 ml of lead-bismuth carrier and cover with a teflon watch glass.

(3) In a perchloric acid fumehood, digest at 100°C on the teflon coated hot plate until sample dissolves.

(4) Remove watch glass and evaporate to perchloric acid fume.

(5) Wash down the walls with 5 ml of 18M H_2SO_4, mix and fume for 10-15 minutes. At this time, the solution no longer wets the sides of the beaker and rolls around the bottom of the beaker like a pool of mercury. The solution can be poured out quantitatively without rinsing.

(6) Roll the solution around to collect isolated droplets and pour into a 250-ml Erlenmeyer flask containing 2 g of anhydrous Na_2SO_4 and 5 g of anhydrous K_2SO_4.

(7) Quickly evaporate over a blast burner to a clear pyrosulfate melt. Cool.

(8) Add 20 ml of boiling 3M HCl, swirl and boil for 5 minutes. Cool.

(9) Either add 50 ml of 3M HCl and 35 ml of deionized water to a final volume of 105 ml in 2M HCl and proceed to Pb-210 determination, or dilute to 50 ml with deionized water and proceed to Ra-226, isotopic thorium, total thorium, isotopic uranium and total thorium determination.

2. Determination of Ra-226, Uranium, Thorium, and Pb-210

2.1 Radium-226, Uranium and Thorium

These radionuclides can be sequentially separated from the solution obtained by potassium fluoride-pyrosulfate fusion. As shown in Figure 2, Ra-226, thorium, actinides and lanthanides are separated from the gross constituents by coprecipitating with lead sulfate. The latter is dissolved in an alkaline solution of diethylenetriaminepentaacetic acid (DTPA), small amounts of barium carrier are added to coprecipitate Ra-226 with barium sulfate by lowering the pH to 4.8. The barium sulfate is filtered onto a membrane filter and the Ra-226 is determined by high resolution alpha spectrometry.[87]

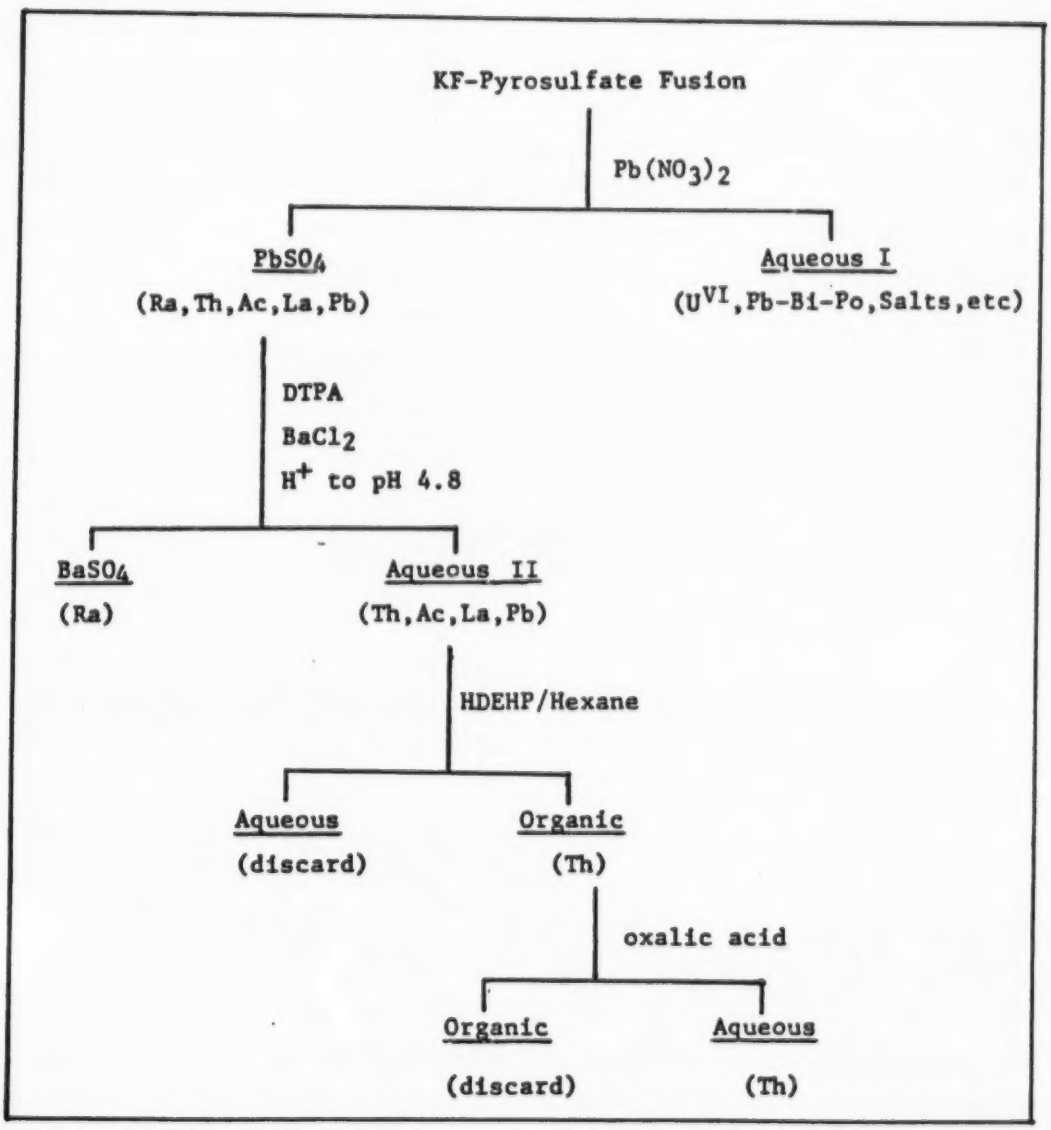

Figure 2: Schematic Separation of Ra-226, Uranium and Thorium

Thorium contained in the DTPA solution (from the separation of barium sulfate, aqueous II) is extracted into a solution of bis(2-ethylhexyl)phosphoric acid (HDEHP) in hexane. It is then extracted back into an aqueous solution of oxalic acid and determined by spectrophotometry after complexing with arsenazo II.[87] If thorium isotopes are required, coprecipitation of thorium with cerous hydroxide, is done and the isotopes determined by high resolution alpha spectrometry.[87]

For the determination of uranium, the solution remaining after the separation of lead sulfate (aqueous I) is evaporated and carried through to a pyrosulfate fusion. The resulting fusion cake is dissolved in nitric acid, the uranium is extracted into ethyl acetate. The uranium content is determined by fluorometry.[87]

2.2 Lead-210

This radioisotope is determined using the solution obtained by $HF/HNO_3/HClO_4$ digestion-pyrosulfate fusion. Since Pb-210 is a low energy (0.018 MeV) beta-emitter, it is determined indirectly via its high energy beta-emitting daughter Bi-210 (1.17 MeV, half-life 5 days). Bismuth-210 is separated from Pb-210 and other constituents in the solution by extraction into a solution of diethylammonium diethyldithiocarbamate (DDTC) in chloroform (Figure 3). The chloroform is removed by evaporation and any organic residue is oxidized with nitric acid. Bismuth-210 is coprecipitated with bismuth hydroxide, and later as bismuth oxychloride, BiOCl, and determined by beta counting.[87,88]

2.3 Radium-226, Uranium, Thorium and Pb-210

These radionuclides can be sequentially separated from the solution obtained by $HF/HNO_3/HClO_4$ digestion-pyrosulfate fusion. As shown in Figure 3, Ra-226, thorium, actinides (except uranium) and lanthanides are coprecipitated with barium sulfate (do not use lead sulfate in this procedure, compare 2.1 above). The barium sulfate precipitate is filtered and dissolved in an alkaline solution of diethylenetriaminepentaacetic acid. Radium-226 is preferentially re-precipitated from solution with barium sulfate by lowering the pH to 4.8. Due to the larger quantity of barium sulfate used, the Ra-226 content cannot be determined by high resolution alpha spectrometry. Radon emanation[87] or gross alpha counting[88] must be used.

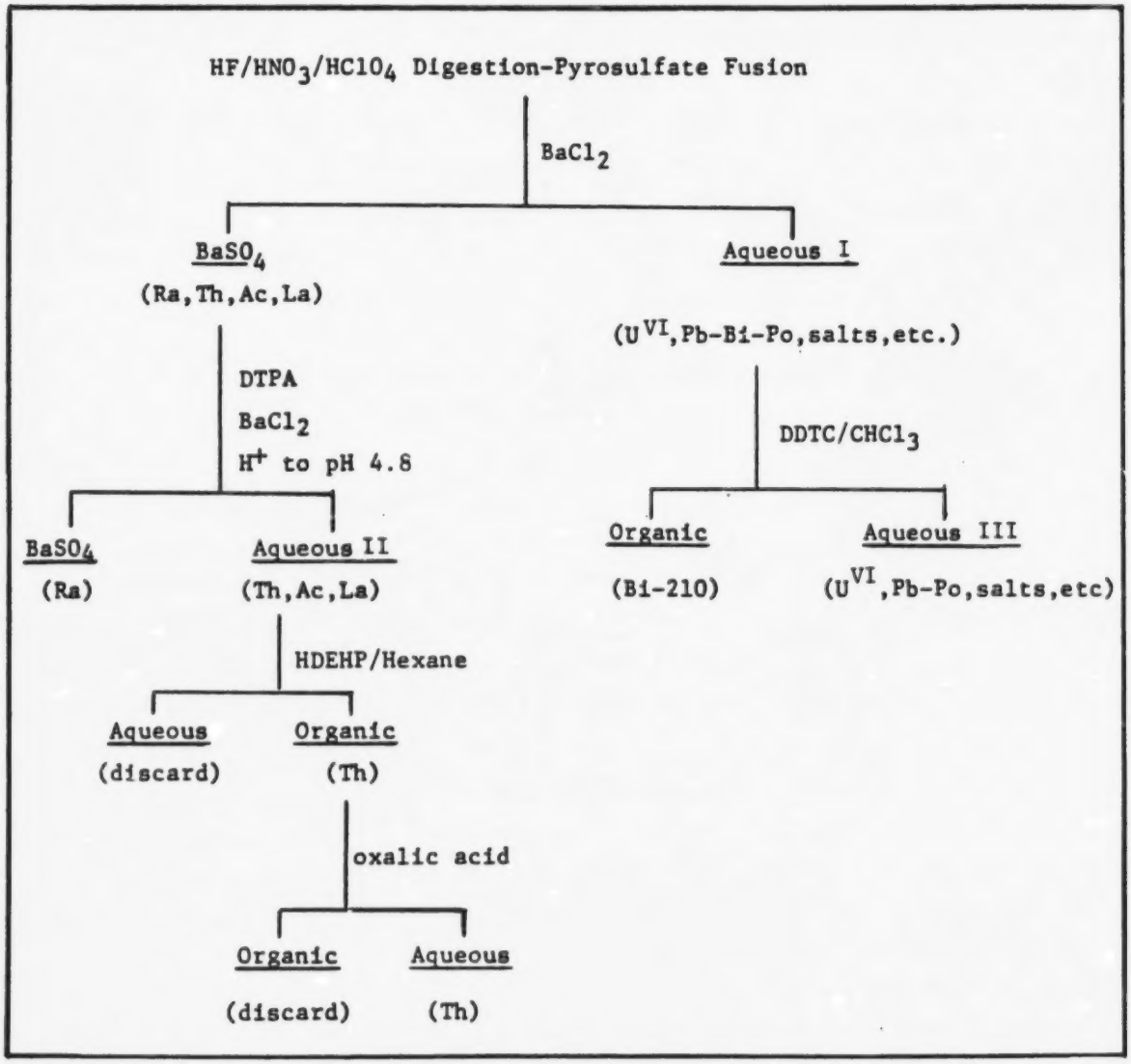

Figure 3: Schematic Separation of Ra-226, Uranium, Thorium and Pb-210

Thorium is determined in the solution obtained after the separation of barium sulfate at pH 4.8 (aqueous II). The procedure is as described in 2.1 above.

For the determination of Pb-210, the aqueous solution (aqueous I) is analysed using the Pb-210 procedure described in 2.2 above. For the determination of uranium, aqueous solution (aqueous III) resulting from the extraction of Bi-210 is evaporated and subjected to pyrosulfate fusion. The fusion cake is dissolved in nitric acid. The uranium content is determined using the extraction procedure described in 2.1 above.

E. SUGGESTION FOR FURTHER WORK (PHASE II)

The following expermental study is suggested as a follow up of this report and as a means of confirming the conclusions drawn here·

(1) Four sample attack procedures should be tested and compared. These procedures are sodium carbonate fusion, $HF/HNO_3/HClO_4$ digestion, $HF/HNO_3/HClO_4$ digestion-pyrosulfate fusion and potassium fluoride-pyrosulfate fusion.

(2) Any insoluble residue remaining from the sodium carbonate fusion or $HF/HNO_3/HClO_4$ digestion should be separated, treated by the potassium fluoride-pyrosulfate fusion and analysed as a separate sample. Each sample should be analysed for U, Th-232, Th-230, Th-228, Ra-226 and Pb-210.

(3) Five soil and mineral samples from AECB and two standard samples are to be run simultaneously. These two standards should include the pitchblend from US Environmental Protection Agency (Las Vegas) and one of the CCRMP or NUTP standards.

(4) Six to ten replicates should be treated by each sample attack procedure and analysed by the recommended procedures to allow statistical calculation.

(5) It is suggested that one or two AECB personnel be present during the latter stages of this phase II work. The purpose of their presence will be to observe the techniques required to carry out the sample dissolution procedures and the importance of the meshing of the analytical procedures with the sample dissolution step.

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